The preparation of metal-polymer composite materials using ultrasound radiation

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Ultrasound radiation is used to prepare a composite material made of polymethylacrylate and amorphous iron nanoparticles. Two preparation methods are described, in which the monomer, methylacrylate, is the starting material. The magnetic properties of the composite material are measured and reveal a superparamagnetic behavior.

I. INTRODUCTION

The propagation of ultrasound waves through a fluid causes the formation of cavitation bubbles.[1] The collapse of these bubbles, described as an implosion in the hot-spot theory, is the origin of extreme local conditions: high temperatures (5000–25000 K) and high pressures (1000 atm).[1] The cooling rates obtained during the collapse are greater than 10^7 K/s.[2,3] These high cooling rates have been utilized by Suslick and his co-workers in sonicating $Fe(CO)_5$ as a neat liquid or in solution,[2,3] where amorphous iron nanoparticles were the sole reaction products. Suslick *et al.* have also prepared amorphous Co[4] and an amorphous Fe–Co alloy.[5] Following Suslick's method, we have reported on being able to control the particle size of the amorphous iron nanoparticles by varying the concentration of $Fe(CO)_5$ in its solution.[6] We have also prepared amorphous Ni[7] and amorphous Fe_2O_3,[8] all having nanometer size particles.

The application of high intensity ultrasound radiation in polymer chemistry has been an active research area.[9,10,11] Most of the published work in this area has been concerned with the degradation of the polymer, where its molecular weight is reduced by sonication in dilute solutions.[10] The first polymerization reaction synthesis using ultrasound radiation was that of acrylonitrile in aqueous solution.[12] Two groups, Kruus and his co-workers and Price and his co-workers, have published most of the work in this field. Kruus has studied the polymerization of nitrobenzene,[13] methyl methacrylate,[14,15] bromobenzene,[15] isoprene,[15] and styrene,[15,16] while Price's favorite molecule has been methyl methacrylate.[17,18]

The preparation of polymer films containing dispersed metallic clusters or metallic colloids has been of great interest,[19–25] because of both its practical and fundamental importance. Griffiths[25] claims that the potential use of colloidal iron dispersions in polymers lies in magnetic recording devices and pigments. The application of polymers containing dispersed metallic clusters to catalysis was the motivation for all the electrochemical studies.[19–24] Apart from their useful catalytic activity toward technologically important substrates, they provide unique opportunities for exploring novel types of catalyst-support interactions.

The two main techniques employed in the preparation of the metal-polymer composites are electrochemical methods and thermolysis techniques. Rajeshwar and co-workers[26,27] have modified the electrochemical method and succeeded in dispersing nanometer size Pt particles in polypyrrole thin films. The platinum colloidal particles are apparently electrotrapped within the growing polymer matrix, affording a three-dimensional array within it.

The earliest report of the preparation of colloidal dispersed polymers using thermolysis as the synthetic method was by Thomas.[28] His synthetic mixture involved dicobalt octacarbonyl dissolved in a hydrocarbon solvent (toluene, for example) containing the polymeric material. Two attempts to disperse iron nanoparticles in various polymers are known to us, the first, by Griffiths[25] and his co-workers, and the second by Smith and Wychick.[29] The iron source in both cases was $Fe(CO)_5$, and a variety of polymers were experimented with. The temperature in Griffiths'[25] experiments was 150 °C, while Smith used 130–160 °C as his temperature range. In both cases, stable colloidal dispersions of zero-valent iron nanoparticles (10–20 nm diameter) were obtained. The magnetic properties show a strong dependence on the particle size.[25] Tennenbaum and her co-workers[30] have also prepared metal-polymer composites by thermal and oxidative decomposition of $Fe(CO)_5$ and $Co_2(CO)_8$ in a poly(vinylidene fluoride) matrix. The most recent work is by Register and his group.[31] They have demonstrated the formation of 10 nm β–Co particles in a polymeric matrix. The method was thermolyzing films of poly(acrylonitrile) containing homogeneously distributed $[Co(dimethylformamide)_6^{+2}] [Co(CO)_4^-]_2$. The size of the cobalt particles can be controlled[31] by varying the thermolysis condition and the loading of cobalt in the films prior to thermolysis.

The most recent work has reported[35] the preparation of freestanding copolymer films containing magnetic iron oxide nanoclusters by static casting. The size distribution of the nanoclusters was relatively narrow, and they were uniformly distributed within the films. Magnetic measurements revealed that the nanocomposite films are superparamagnetic.

In the current investigation we have combined the two sonochemical methods, polymerization and creation of amorphous metallic nanoparticles, to create a metal-polymer composite material. In this paper we report on the preparation of a methylacrylate-iron composite by sonochemical methods. The products were chemically analyzed for their iron content. Their molecular weight, morphology, and magnetic properties were also studied.

II. EXPERIMENTAL

Two experimental methods have been employed for the preparation of the composite material. In the first, $Fe(CO)_5$ and distilled methylacrylate were sonicated as a mixture of neat liquids, 35 ml of a 1.25% (by weight) mixture of iron pentacarbonyl in methylacrylate were deoxygenated by bubbling argon through the liquid for 20 min and then irradiated under an argon flow of 100 ml/min at 1 atm with a high intensity ultrasonic probe (Sonics and Materials, VC-600, 20 kHz, 100 W/cm^2 [38]). During the sonication, the glass cell was wrapped in a dark cover to avoid photopolymerization. After 30 min of irradiation (avoiding degradation) at a dry ice–acetone temperature, the solution was treated with cold methanol, precipitating the polymeric product. In the second method, amorphous iron nanoparticles were prepared following Suslick's recipe.[2,3] The dried amorphous iron powder was introduced into the sonication cell without exposure to air and mixed with a solution of the methylacrylate monomer in N,N′-dimethylformamide (DMF). The concentration of the methylacrylate solution in DMF was 5.5 M. 35 ml of this solution was mixed with various amounts of amorphous iron nanoparticles. The amounts of the iron powder were changed from 50 mg to 200 mg. The solution was sonicated for 90 min under an argon flow of 100 ml/min at 1 atm at a dry ice–acetone temperature. The product of the sonication was a colloidal solution that was stable for at least a month. The polymer was precipitated from the colloidal solution in the following way. An excess of cold methanol was added to the solution by the end of the sonication. The precipitate was dried in vacuum at room temperature overnight. It was then subjected to various examinations. The first was the determination of its molecular weight. This was carried out using a GPC (Thermo Separation Products, AS100) instrument. The polymethylacrylate was dissolved in chloroform (10 mg/ml) prior to its injection into the GPC column.

The column used was phenogel heated to 35 °C. A Shodex, RI-71 refractive index detector was employed in these experiments. The composite material containing the iron was then treated in the following way prior to its introduction into the GPC. The material was dissolved in acetone, and untrapped iron was precipitated and removed from the solution. To the acetone solution an excess of cold methanol was added, precipitating the polymer. The polymer was dried in vacuum overnight, redissolved in chloroform (10 mg/ml), and injected into the GPC.

The AFM measurements were carried out at contact mode employing a Topometrix TMX2010 Discoverer, using an 8 μm tube scanner and tips with a cantilever having a spring constant of 0.032 N/m. Two types of pictures are presented in this investigation, one depicting the topography of the composite material, the other measuring the lateral force. The sample preparation was carried out in the following way. The solution of the composite material was spread on a flat mica surface. Cold methanol was then dropped onto the surface, causing the precipitation of the polymer on the mica. Transmission electron micrographs were obtained with a JEOL-JEM100SX electron microscope. Magnetization loops were measured at room temperature, using a VSM, Oxford Instrument Vibrating Sample Magnetometer.

III. RESULTS AND DISCUSSION

The chemical analysis results of polymers prepared by the two methods are presented in Table I. The results according to Table I indicate that it is easier to introduce the iron by starting with amorphous iron as the precursor than it is with $Fe(CO)_5$. The percentages presented in Table I are weight percentages of the iron in the mixture of $Fe(CO)_5$ and methylacrylate (first row, first column) in the starting solution. The second row presents the weight percent of iron in the starting solution (first column) and in the composite material (second column). We have also examined the possibility of irradiating the $Fe(CO)_5$ with methylacrylate at lower intensities of ultrasound power and have obtained a lesser amount of iron in the polymer.

Molecular weights of the polymers are presented in Table II. When the Mn values of the polymeric composite material are compared with those of the polymeric product obtained from the irradiation of the monomer alone at the same irradiation time and concentration of

TABLE I. The concentration of iron in polymers prepared by the two methods.

Starting materials	% Fe in starting solution	% Fe in final product
Methylacrylate–Fe(CO)$_5$	0.50	0.56
Methylacrylate (DMF)–50 mg amorphous Fe	0.3	5.4

TABLE II. Molecular weights of polymers obtained from various sonications.

| Monomer	Sonication time (min)	M_n
Methylacrylate	30	134000
Methylacrylate in DMF	90	176000
Methylacrylate in DMF containing 50 mg Fe	90	142000

FIG. 1. AFM topographic image of a polymethylacrylate-iron composite material, which was prepared by sonicating 50 mg of amorphous iron with 35 ml of 5.5 M solution of methyl acrylate in DMF for 90 min.

the monomer, a 20% reduction in the molecular weight is detected. This can be ascribed to the influence of the iron in the growth of the polymer. This would mean that the recombination of the iron pentacarbonyl dissociation products disturbs the growth of the polymeric radical. Thus the dissociation products serve as a quenching agent for the creation of the polymer.

We have already pointed out the formation of a colloidal solution as the sonication product. This solution was stable in air for about two months, and we could not detect any precipitate form. It is worth noting that this result, which is of great technological importance in the field of magnetic fluids, accords with recent results reported by Suslick.[32] In his work, $Fe(CO)_5$ was sonicated with a PVP (polyvinylpyrolidone) polymer (average MW of 40000), yielding a colloidal solution of the amorphous iron in the polymer. Leaving the composite material in solution or as a precipitated solid in air for few days causes the oxidation of the iron to Fe^{+3}. The oxidation state of the oxidized iron was determined by Mössbauer spectroscopy.

A. Morphology: AFM and TEM measurements

In Fig. 1, an AFM image of the particles of the composite material are depicted. This picture images the topography of the particles. It identifies particles whose sizes vary between 600 nm and 4 μm protruding from the surface. We can also identify some 100 nm nuclei on or near the boundaries of the particle. Some of these nuclei can be found spread all over the polymer and also on the substrate surface. The careful study of the lateral image presented in Fig. 2 reveals significant differences in the friction between the valley areas and the hilly areas. Another location where these friction differences are observed is at the 100 nm nuclei. These nuclei are assigned as the iron particles. This assignment is proposed based on the topography, as well as the lateral pictures. Three areas are identified, the lower altitude areas which are attributed to the substrate areas, the higher altitude places which are the polymer locations, and the iron nuclei. The iron particles can be observed inside the polymer, on its surface, and at the polymer edges. The reason why they are observed more clearly at the polymer edges has to do with the gradual slope of the edges of the polymeric areas.
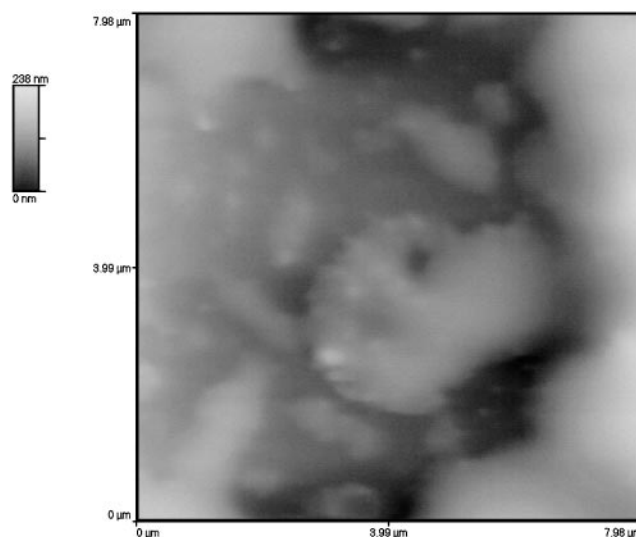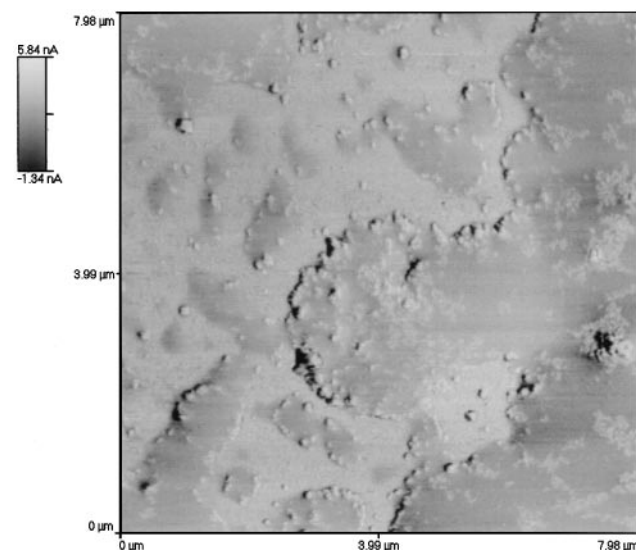

FIG. 2. AFM lateral force image of the same composite material as in Fig. 1.

To compare the behavior of the polymer with the composite material, we present in Fig. 3 the AFM image of the unperturbed polymer. The figure presents the topography of the polymer. It reveals that the adhesion forces of the polymer are different from those of the composite material toward the mica substrate. For the polymer, these forces are stronger, and a better unified coverage of the substrate is observed. The protruding islands observed for the composite material, attributed to the iron clusters, are missing in the polymer picture.

In Fig. 4 we present the TEM picture of the same composite material as in Fig. 1. It clearly shows the
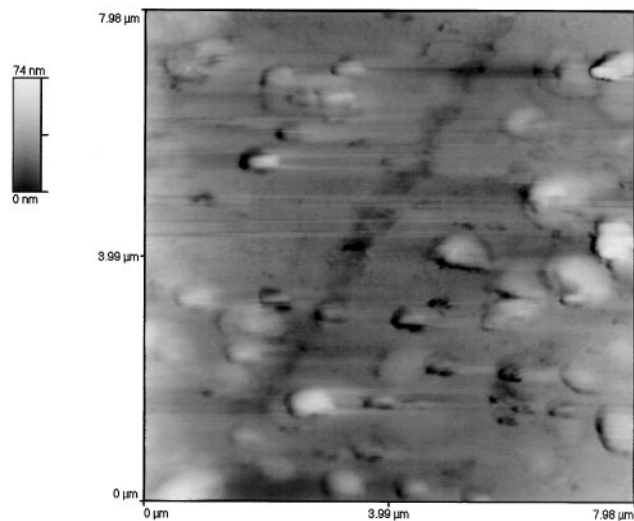
FIG. 3. AFM topographic image of a polymethylacrylate that was prepared by sonicating 35 ml of a 5.5 M methyl acrylate solution in DMF for 90 min.
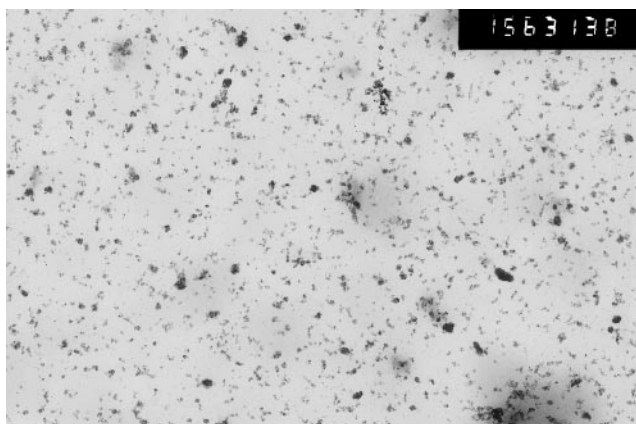

FIG. 4. Transmission electron micrograph picture of the same composite material as in Fig. 1. The magnification power is 15000.

dispersion of the iron particles all over the area. The sizes of the black iron spots are of the same values as in Fig. 1. The shape of the polymer particle is somewhat less distinct; however, a careful look at the picture will identify the grain boundaries. The amorphous nature of the iron particles is demonstrated in Fig. 5, where the electron diffraction patterns are presented. The picture shows only ring patterns and the absence of discrete spots.

B. Magnetization measurements

Magnetic measurements were carried out for all the samples. The polymer that was prepared by the first method, namely by ultrasound irradiation of a mixture of methylacrylate monomer and ironpentacarbonyl, showed zero magnetism. This is clearly related to the low concentration of the iron in the polymer (0.56%). The same result was obtained when a low concentration
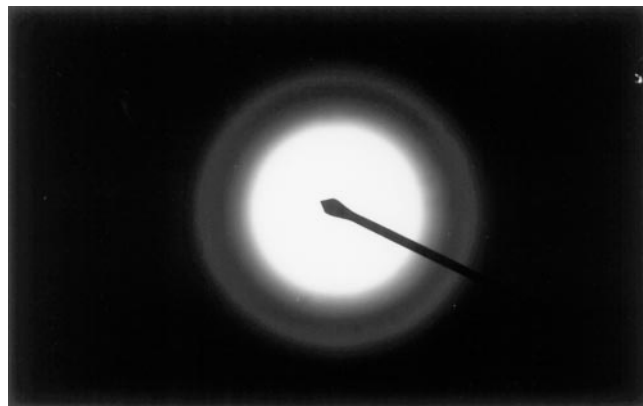

FIG. 5. Electron diffraction patterns of composite material described in Fig. 1.

of amorphous iron was introduced into the sonication cell when the second method was employed. Only when 100 mg of amorphous iron was imbedded in the polymer was a magnetic signal obtained. The signal grew when larger amounts of amorphous iron were used in the starting solutions. In Fig. 6, we present the magnetic loop obtained for a polymer prepared from the irradiation of a methylacrylate solution of 5.5 M in DMF and 100 mg of amorphous iron (0.6% iron and 99.4% methylacrylate by weight). The superparamagnetic nature of the iron particles obtained from the sonication of $Fe(CO)_5$ has been demonstrated by Grinstaff and co-workers.[33] A similar behavior was detected for amorphous nickel,[7] as well as for the amorphous alloy Fe/Ni.[34] Figure 6 shows the magnetization as a function of the applied magnetic field for the above-mentioned sample. The room temperature measurement does not show hysteresis and does not saturate at even 15 kGauss, which is consistent with superparamagnetic behavior. The magnetic moment is 1.5 emu/gr at 15 kG. A larger magnetic
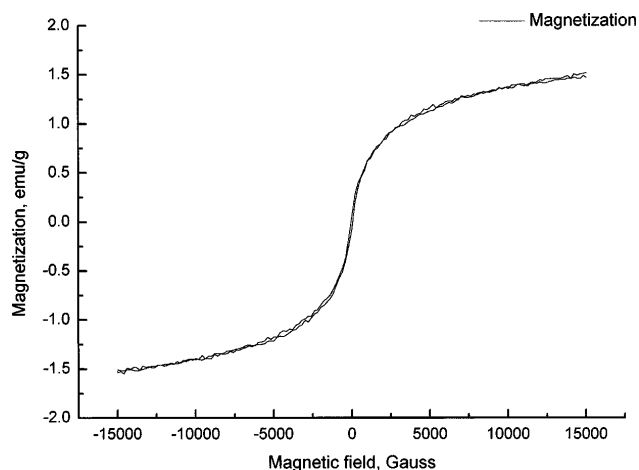

FIG. 6. The room temperature magnetization loop of a composite material prepared by sonicating 100 mg of amorphous iron with 35 ml of 5.5 M solution of methyl acrylate in DMF.

moment was obtained when the composite material was heated to 270 °C for 17 h in nitrogen. Whether the doubling of the magnetization of approximately 3 emu/g is due to crystallization or whether it is the outcome of an agglomeration of the iron particles is still under study. It is worth noting, however, that if the composite material was prepared from crystalline iron nanoparticles (preheating of the amorphous iron to 350 °C for 4 h, in vacuum), the product contained a very small amount of iron. This is another demonstration of the large reactivity of the amorphous iron nanoparticles.[12] We have detected similar behavior in the coating of the iron nanoparticles by octadecane thiol, where the amorphous iron was fully coated and the crystalline form was hardly touched by the surfactant.[36] Similar differences were found by Suslick and his group,[37] where the catalytic activity of amorphous iron deposited on SiO_2 was found to be 5–10 times stronger than the corresponding crystalline iron. These differences were observed for the Fischer–Tropsch reaction.

C. The stability of the composite material: TGA measurements

To obtain some information on the stability of the polymer and the effect of the iron on its stability, we have carried out thermogravimetric analysis measurements. In Figs. 7 and 8 we present the TGA spectra of the polymethylacrylate prepared by the irradiation of methylacrylate in DMF for 90 min, and that of the composite product prepared by sonicating 50 mg of amorphous iron with methylacrylate in DMF for the same time, respectively. The polymer disintegrates at 414 °C, while the composite material is stable only to 349 °C. We could detect a gradual decrease in the decomposition temperature as the amount of the iron in the polymer increased. Our explanation for this dependence is as
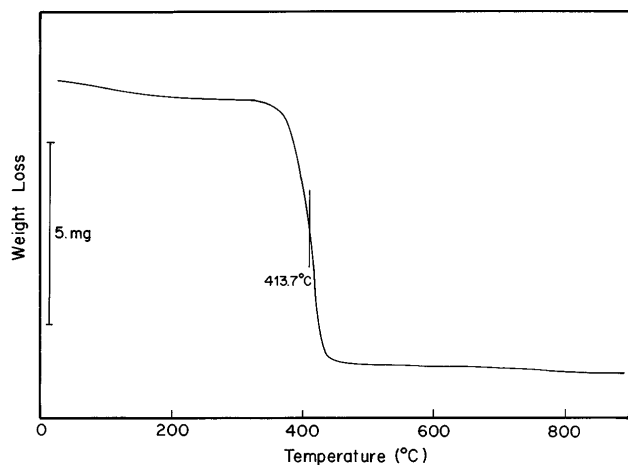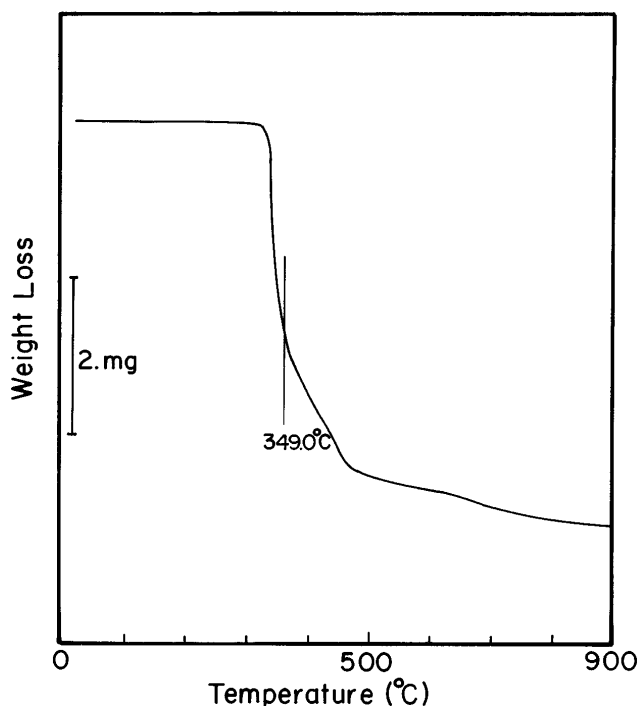

FIG. 8. The TGA spectrum of the composite material prepared as in Fig. 1. The heating rate was 10°/min.

follows: the perturbation that the iron introduces affects the three-dimensional structure of the polymer. This perturbation weakens the van der Waals interactions between the polymer chains, thus affecting the stability of the polymer, which is reflected in the lowering of the decomposition temperature.

IV. CONCLUSION

This manuscript reports the use of ultrasound radiation for the preparation of a metal-polymer composite material. Two methods of preparation are described. In one of these methods the concentration of the metal in the polymer was sufficiently large so that the magnetic properties of the composite material were amenable for experimental observation.

ACKNOWLEDGMENTS

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FIG. 7. The TGA spectrum of polymethylacrylate prepared as in Fig. 3. The heating rate was 10°/min.

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